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(54) OIL-IN-WATER EMULSIONS WITH IMPROVED BACTERIA-RESISTANCE

(71) We, EXXON RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to oil-in-water emulsions, more especially to such emulsions (i) for use as, or in, anti-corrosion compositions and hydraulic oils; and (ii) use in metal-working processes. The invention further relates to synergistically active bactericidal additive mixtures and concentrates suitable for use in such emulsions.

Oil-in-water emulsions are widely used for many purposes. For example they are employed in metal working process, such as machining (i.e. with production of chips, swarf etc.) and in shaping (i.e. without production of chips, swarf etc.). The emulsions are normally collected after use (or the aqueous and oil phases are collected if separation has occurred) and, after separation of contaminant metal, recirculated (after re-emulsification if phase separation has occurred) for further use.

During extended use of the emulsion (especially in metal-working processes, where it will be re-used many times) microbial contamination tends to occur. The effects of such contamination are well-known, especially in metal-working processes. For example the emulsions may become discoloured, an objectionable odour may be produced, and a corrosion problem may arise due to a fall in pH of the emulsion. The stability of the emulsion may also be affected, and droplet size increase so caused can be disadvantageous to tool life and the surface of the metal being worked.

In the past it has been the practice to attempt to protect such emulsions against bacterial degradation by the use of a water-soluble bactericide. However, even though some of these bactericides are quite effective they can give rise to skin irritation in machine operators. Furthermore, they may have a toxicity such that a maximum concentration in the emulsion may be imposed by Health or other Authorities; and this maximum may be insufficient for effective bactericidal action.

According to a feature of the present invention, a bactericidal additive concentrate for use in a metal-working composition, a corrosion-inhibiting composition or an hydraulic oil, comprises 99.75 wt% to 95 wt % of a vehicle which is a mineral oil optionally containing one or more components selected from known emulsifiers, solubilizers, extreme-pressure additives and corrosion inhibitors, and 0.25 wt % to 5.0 wt % in total of at least one water-soluble bactericide (*A*) and at least one oil-soluble (but substantially water-insoluble bactericide (*B*); the weight ratio of total (*A*) to total (*B*) being greater than 1:1 but less than 20:1.

It has been unexpectedly found that by employing both types of bactericides, in the proportions stated, a surprising synergistic effect is obtained in the anti-bacterial protection given, for example, to an aqueous metal-working lubricant emulsion. Normally, the most advantageous effect is obtained when the said ratio is in the range 5:1 to 15:1, particularly 9:1 to 12:1.

Preferably, the invention employs as water-soluble bactericides those that release formaldehyde. Examples of such are: 1,3,5-trialkyl hexahydro - (s) - triazines,

the alkyl groups (preferably C_1 up to C_5 or C_6, or cycloalkyl) may be the same or different. Examples are the triethyl; the diethyl, mono n-butyl and the monoethyl di n-butyl compounds. Also one or more of the alkyl groups may be hydroxy-substituted. Especially suitable is the hexahydro-1,3,5-tris(2-hydroxyethyl)-(S)-triazine compound. A mixture of an aryl methanol (such as benzyl alcohol) compound and chloral formamide is also an effective formaldehyde-releasing mixture.

Other water-soluble bactericides which may be employed are the non-formaldehyde-releasers, as represented by, for example, 1,2-benzisothiazolone; a 6-acetoxy-2,4 dialkyl-*m*-dioxane, especially the dimethyl and diethyl compounds; 2-methyl 4-isothiazoline-3-one and/or 5-chloro 2-methyl 4-isothiazoline-3-one; sodium salt of 2-pyridine-N-oxide thione; and 12-mercapto-pyridine or the alkali metal or ammonium salt thereof.

The preferred oil-soluble, substantially water-insoluble, bactericide is a phenolic compound. The preferred such compound is 2-phenyl phenol. This compound has a water-solubility of only about one part in six-thousand at 25° C. In general the water-solubility of the oil soluble bactericides used in the invention will not normally exceed 1 part in 3000, at 25° C. Other examples of this phenolic type of bactericide are *o*-benzyl-parachlorophenol, chloro 2-phenylphenol and laurylpentachlorophenol. Further examples, but much less preferred, are chlorocresols.

A very effective mixture is (by weight) 45% of hexahydro-1,3,5-tris (2-hydroxyethyl)-(s)-triazine, 45% of 1,2-benzisothiazolone and 10% of the oil-soluble compound. In parts by weight this is substantially 1:1:0.2 and is a ratio of water-soluble: oil-soluble of 10:1. Other suitable mixtures of the said compounds in ratio 7:1 or 14:1. Yet another suitable mixture is of said triazine, the sodium salt of 2-pyridine-N-oxide thione and said oil-soluble compound, preferably in wt. ratio 7:3:1, that is water-soluble: oil soluble ratio 10:1. Still another suitable mixture is one which contains the said triazine, the said phenolic compound, and a mixture of (a) 2-methyl, 4-isothiazoline-3-one and (b) 5-chloro, 2-methyl 4-isothiazoline-3-one; a suitable wt. ratio being 8 to 10 triazine: 1 phenolic compound: 0.5 to 1 of mixture (a) plus (b).

An additive concentrate of the present invention, for use in forming an aqueous, metal-working, lubricant emulsion, normally contains 0.5% to 2.0 wt, preferably 0.9 to 1.5 wt. %, in total of the aforesaid additives, dissolved or dispersed in 99.5 to 98 wt. % preferably 99.1 to 98.5 wt. % of a vehicle essentially consisting of a mineral oil (suitably a naphthenic oil may be paraffinic) having a preferred viscosity in the range 30—600 SSU at 38° C, especially 30—110 SSU; said oil may contain minor proportions of emulsifiers, for example petroleum sulphonates, glycol ethers; solubilisers such as butyl alcohol, glycol, oleic acid; extreme pressure additives such as phosphates, zinc dialkyl dithiophosphates, chlorinated wax hydrocarbons and sulphurised compounds; and corrosion inhibitors such as amine-type compounds.

The invention also provides, in accordance with a still further feature, a lubricant for use in metal-working processes, essentially comprising an aqueous emulsion containing up to 10 vol. %, suitably up to 5 vol. % preferably 0.5 to 5 vol. %, advantageously 3 to 4 vol. % of the aforesaid additive concentrate. By combining these quantities with the aforesaid additive concentrates it will be seen that the aqueous emulsion can contain up to a total of 5000, and suitably up to 2500, parts per million by wt. of bactericides, in which the wt, ratio water-soluble to oil-soluble will be in the stated range 1:1 to 20:1. With the preferred 3 to 4 vol % of the preferred 0.9 tc 1.5 wt. % concentrate the range will be from 270 to 600 ppm. It is to be understood, however, that the invention includes within its scope emulsions having these stated total quantities of bactericides (in the stated range 1:1 to 20:1) whether prepared from the concentrates just described, or whether prepared from the individual bactericide components.

The following Examples illustrate, in a non-limitative manner, various features of the invention, and contain comparative matter where indicated.

In the Examples the water-soluble bactericides employed are all commercially available and are designated *A* to *H*, and the oil-soluble bactericide, again commercially available, is designated *J*.

Bactericides *A* and *C* are essentially the specific hexahydro tris triazine compound aforespecified. *B* is 1,2-benzisothiazolane. *D*, *E*, *F* are all commercially available bactericidal hexahydrotriazine derivatives. *G* is the aforespecified formaldehyde-releasing mixture. *H* is 6-acetoxy-2,4-dimethyl-*m*-dioxane. The oil-soluble bactericide *J* is 2-phenyl phenol.

Furthermore, in the Examples, the Warburg test referred to is as follows: an emulsion is prepared with sewage water and brought into a closed system in which KOH absorbs all carbon dioxide. As bacteria produce CO_2 and consume O_2 the pressure serves as a tool to evaluate microbiological activity. The minimum concentration of an emulsion concentrate which safely protects the prepared emulsion for 100 hours against decomposition by microbes (pressure drop less than 20 mm) is noted as critical concentration (the lower the better). It will be appreciated that this is a laboratory-scale test (although its results are fully reflected in large-scale practice), and thus the emulsions employed contain only up to about 2 vol. % of the additive concen-

trate (mineral oil, conventional additives and bactericides).

The Warburg test is described in the literature for example in Werkstoffe und Korrosion *1964*, No. 1 pp. 59—63.

The Germ Number is obtained by preparing some emulsions in the same way as for the Warburg test but not in a closed system. After preselected periods of time a sample is taken and the germ number is determined. The germ number is plotted vs. time. The time is recorded where the critical number of 10^6 germs/ml are reached. The longer the time taken to reach this level the better.

Finally, in the Examples the base composition to which the bactericides were added was a composition containing a major proportion (approximately 85%) by wt. of a naphthenic mineral oil of viscosity about 100 SSU at 38° C, approximately 10 wt. % of petroleum sulphonates and a total of approximately wt. % of conventional solubilisers, extreme pressure additives and corrosion inhibitors.

This composition is hereafter designed "Base Composition" in the Examples.

Example 1.

Table 1 shows for comparative purposes the Warburg test results (a) using only the water-soluble bactericides, as in known practice; and (b) when an oil soluble bactericide alone.

Table 2 shows the Warburg test results when employing combinations according to the invention.

Underneath Table 2 some comparisons are made between the results in that Table and in Table 1.

Other comparisons which can be made in respect of total quantity of active material (that is bactericide) required to obtain acceptable results. Thus, for example 137 parts per million of *A* plus *J* are as effective as 175 parts of *A* alone. It should be noted that *J* alone fails even at 200 ppm. Again *D* and *J* each fail separately at 200 ppm, but even at 165 ppm. combined begin to approach satisfactory results.

Example 2.

Table 3 shows the effect of increasing the ratio of water soluble: oil soluble bactericides to 20:1. The result is unacceptable.

Table 4 below shows the effect of increasing the ratio to 1:1. Again the result is unacceptable. The Table also shows that when the oil-soluble compound is used alone it is impossible to pass the Warburg test even at 2 vol. %.

TABLE 4

Base oil (wt.%)	99	99	99	99	98
A (wt.%)	1	0.9	0.5	—	—
J (wt.%)	—	0.1	0.5	1	2
Minimum emulsion concentration (vol. %) to reach the 100 hr. figure in the Warburg test	1.75	1.50	>2.00	>2.00	>2.00

Example 3.

Tables 5 and 6 show results of Germ Number tests and also incorporate Warburg test results from previous Tables.

Example 4.

Table 7 shows the results of employing a 4 vol. % emulsion in continuous operation until decomposition. This example is an illustration of the use of an emulsion on a commercial scale. It will be seen that the emulsions containing bactericides in accordance with the invention have vastly superior endurance.

TABLE 1

Efficiency of Bactericides

Hours to 20 mm Pressure Drop in the Warburg Test

Base Composition	wt.%			99.0				
Bactericide	wt.%			1.0				
Parts per million bactericide present		50	75	100	125	150	175	200
Emulsion Concentration	Vol.%	0.50	0.75	1.00	1.25	1.50	1.75	2.00
A	hrs.	–	–	21	36	64	>100	>100
B	hrs.	–	–	68	>100	>100	>100	>100
C	hrs.	–	–	33	33	64	>100	>100
D	hrs.	–	–	<20	<20	<20	<20	<20
E	hrs.	–	–	<20	<20	<20	<20	<20
F	hrs.	–	–	<20	<20	<20	<20	<20
G	hrs.	–	–	<20	<20	22	24	25
H	hrs.	–	–	<20	<20	<20	<20	<20
0.5 *A*+0.5 *B*	hrs.	35	49	>100	>100	>100	>100	>100
0.7 *A*+0.3 *B*	hrs.	25	25	44	51	>100	>100	>100
0.1 *J* (99.1 base composition) (10 parts per million present)	hrs.	–	–	<20	<20	<20	<20	<20
2.0 *J* (98 base composition) (200 parts per million present)								<100

TABLE 2

Efficiency of Combination of Oil—and Watersoluble Bactericides

Hours to 20 mm Pressure Drop in the Warburg Test

Base Composition	wt.%	98.9					
Bactericides	wt.%	1.1					
Emulsion Concentration	Vol.%	0.50	0.75	1.00	1.25	1.50	2.00
Part per million bactericide present		55	82	110	137	165	220
A 1.0 wt.%, *J* 0.1 wt.%	hrs.	—	—	32	>100	>100	>100
B 1.0 wt.%, *J* 0.1 wt.%	hrs.	27	44	>100	>100	>100	>100
A 0.5 wt.%, *B* 0.5 wt.%, *J* 0.1 wt.%	hrs.	42	>100	>100	>100	>100	>100
D 1.0 wt.%, *J* 0.1 wt.%	hrs.			<20	<20	48	>100

Improvements by the addition of 0.1 wt.% *J* to:—

A (1.0 wt.%) Minimum Emulsion Concentration for 100 hrs. Reduced from 1.75 to 1.25 wt.%

B (1.0 wt.%) Minimum Emulsion Concentration for 100 hrs. Reduced from 1.25 to 1.00 wt.%

A+*B* (0.5+0.5 wt.%) Minimum Emulsion Concentration for 100 hrs. Reduced from 1.00 to 0.75 wt.%

D (1.0 wt.%) At 2 wt.% Emulsion Concentration the 100 hrs. result is only possible with 0.1 wt.% *J* present (compare last line of Table 1).

TABLE 3

Hours to 20 mm Pressure Drop in the Warburg Test

Base Composition	wt.%	98.95				
Bactericides	wt.%	1.05				
Emulsion Concentration	Vol.%	0.75	1.00	1.25	1.50	1.75
Parts per million bactericide present		78	105	131	157	183
A 1.0 wt.%, *J* 0.05 wt.%	hrs.	–	–	34	42	>100
A 0.5 wt.%, *B* 0.5 wt.%, *J* 0.05 wt.%	hrs.	42	68	–	–	–

Deterioration by the addition of only 0.05 wt.% *J*, i.e. ratio *A:J* or (*A+B*):J of 20:1

With *A* (1.0 wt.%) Minimum Concentration Remains at 1.75 Vol.% However Worse Results on 1.25 and 1.50 Vol.%

With A+B (0.5+0.5 wt.%) Minimum Concentration Raised from 1.00 to at least 1.25 Vol.%

TABLE 5

Base Composition wt.%	99.0				98.9				98
A ,,	1.0				1.0				–
J ,,	–				0.1				2.0
Parts per million bactericide	100	125	150	200	110	137	165	220	400
Emulsion Concentration Vol.%	1.0	1.25	1.5	2.0	1.0	1.25	1.5	2.0	2.0
Warburg Test hrs.	21	36	64	>100	32	>100	>100	≥100	<100
Germ Number hours to 10^6 germs/ml	–	[illegible]	70	80	56	126	193	>250	<24

TABLE 6

Base Composition wt.%	99.0				98.9				98
D ,,	1.0				1.0				–
J ,,	–				–				2.0
Parts per million bactericide	100	125	150	200	110	137	165	220	400
Emulsion Concentration Vol.%	1.0	1.25	1.5	2.0	1.0	1.25	1.5	2.0	2.0
Warburg Test hrs.	<20	<20	<20	<20	<20	<20	48	>100	<100
Germ Number hours to 10^6 germs/ml	7	7	7	11	24	24	70	150	<24

TABLE 7

Weeks of Continuous Operation until Decomposition

Test No.			1	2	3	4	5
Base Composition Plus							
A	1.0 wt.%	weeks	3	2	1	3	2
A J	1.0 wt.% 0.1 wt.%	weeks	8	8	–	–	–
A B J	0.5 wt.% 0.5 wt.% 0.1 wt.%	weeks	–	–	10	10	10
J	1.0 wt.%	weeks	<1	<1	<1	<1	<1

WHAT WE CLAIM IS:—

1. A bactericidal additive concentrate for use in a metal-working composition, a corrosion-inhibiting composition or an hydraulic oil; comprising 99.75 wt. % to 95 wt. % of a vehicle which is a mineral oil optionally containing one or more components selected from known emulsifiers, solubilizers, extreme-pressure additives and corrosion inhibitors; and 0.25 wt. % to 5.0 in total of at least one water-soluble bactericide (*A*) and at least one oil-soluble, substantially water-insoluble,

bactericide (*B*), the weight ratio of total (*A*) to total (*B*) being greater than 1:1 but less than 20:1.

2. An additive concentrate as claimed in claim 1, wherein the said ratio is in the range 5:1 to 15:1.

3. An additive concentrate as claimed in claim 1 or claim 2, wherein the said ratio is 9:1 to 12:1.

4. An additive concentrate as claimed in any preceding claim, comprising 0.9 to 1.5 wt. % of said mixture in 99.1 to 98.5 wt. % of said vehicle.

5. An additive concentrate as claimed in any preceding claim, wherein the bactericide (*A*) is a formaldehyde-releasing compound.

6. An additive concentrate as claimed in claim 5, wherein the bactericide (*A*) is selected from 1,3,5 - trialkyl hexahydro - (*S*) - triazines, and hexahydro - 1,3,5 - tris (2-hydroxyalkyl)-(*S*)-triazines.

7. An additive concentrate as claimed in claim 6, wherein the bactericide (*A*) is hexahydro-1,3,5-tris (2-hydroxyethyl)-(*S*)-triazine.

8. An additive concentrate as claimed in claim 1, wherein bactericide (*A*) contains 1,2-benzisothiazolone.

9. An additive concentrate as claimed in any preceding claim, wherein bactericide (*A*) further contains the sodium salt of 2-pyridine-N-oxide thione.

10. An additive concentrate as claimed in any preceding claim, wherein the oil-soluble bactericide (*B*) is a phenolic compound.

11. An additive concentrate as claimed in claim 10, wherein the bactericide (*B*) is 2-phenylphenol.

12. An additive concentrate as claimed in claim 10, wherein the bactericide (*B*) is *o*-benzylparachlorophenol or chloro 2-phenylphenol.

13. An oil-in-water emulsion for use in metal-working operations; containing up to a total of 5000 parts per million by weight of bactericides (*A*) and (*B*), said bactericides and proportions thereof being as defined in any previous claim.

14. An emulsion as claimed in claim 13, wherein said quantity is up to 2500 parts per million.

15. An emulsion as claimed in claim 14, wherein said quantity is from 270 to 600 parts per million.

16. An emulsion as claimed in any one of claims 13 to 15 and prepared from an additive concentrate as defined in any of claims 1 to 12.

17. An emulsion as claimed in any one of claims 13 to 16 and substantially as herein described.

18. An additive concentrate as claimed in any of claims 1 to 12 and substantially as herein described.

19. The use as a lubricant and/or coolant in a metal-working operation of an emulsion claimed in any one of claims 13 to 17.

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